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Reactions of O-atoms and O₂ With Small Carbonaceous Free Radicals

Ghanshyam L. Vaghjiani
ERC
Air Force Research Laboratory
AFRL/PRSA
10 E Saturn Blvd
Edwards AFB, CA 93524
USA

Email: ghanshyam.vaghjiani@ple.af.mil
Tel: 661 275 5657
Fax: 661 275 6245

The interactions of carbonaceous combustion species in rocket plumes with the atmosphere are thought to play an important role in the production of ultraviolet, visible, and infrared radiation signatures at high altitudes. A detailed understanding of the pertinent chemical reactions that produce the electronically excited species, and of the competing quenching reactions that remove the internal energy in radiation-less processes is needed to accurately calculate plume spectral signatures and absolute radiances (in the short wavelength region), and their temporal/spatial evolution in the high atmosphere. To facilitate these efforts, we have carried out laboratory investigations to elucidate the reaction mechanism(s) in the oxidation of CH, CH₂, C₂H, and C₂O with O-atoms and O₂. Sufficient exothermicity in CH, CH₂, and C₂H reactions (except C₂H + O) is available to produce CO in one or more of the triplet states (a, a', and d). Even more reaction enthalpy is available in C₂O reaction(s) to produce higher excited states of CO (e, A, I, and D). Other excited species such as CH(A²Δ) in C₂H plus O or O₂, and OH(A²Σ⁺) in CH + O₂ reactions are also possible. CO-uv chemiluminescence has previously been identified in C₂H + O₂ reaction and both CO-uv and CO-vuv in the C₂O + O reaction. However, no information is available on the product branching ratios of the excited CO states responsible for the emission. Estimates of the branching ratio of CH(A²Δ) formation in the reactions of C₂H with O and O₂ can be found in the literature. To our knowledge, triplet CO formation in CH and CH₂ reactions has not yet been positively identified. Fast discharge-flow tube and pulsed-laser photolysis methods have been employed in this work to study the reaction kinetics and chemiluminescence in these reactions. The experimental approach and results of these studies will be presented.

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